

## DECLARATION

I, Junko Nakamura, of SHIGA INTERNATIONAL PATENT OFFICE, 3-1, Yaesu 2-chome, Chuo-ku, Tokyo, Japan, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No. 11-341442 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This 24th day of November, 2004

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This is to certify that the annexed is a true copy of the following application as filed with this office.

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Mitsubishi Gas Chemical Co., Inc.

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[Title of the Invention] METHOD FOR STARTING METHANOL  
REFORMING APPARATUS AND APPARATUS FOR SUPPLYING FUEL TO SAID  
APPARATUS

[Number of Claims] 4

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[Title of the Invention] METHOD OF STARTING METHANOL REFORMING  
APPARATUS AND APPARATUS FOR SUPPLYING FUEL TO SAID APPARATUS

[Claims]

[Claim 1] A method of starting a methanol reforming apparatus that generates a hydrogen-rich gas by reacting a mixed gas of water, methanol and air on a catalyst, which comprises:

controlling the amounts to be introduced so that the molar ratio of water/methanol is 4.6 or higher and/or the molar ratio of air/methanol is 1.5 or lower.

[Claim 2] A method of starting a methanol reforming apparatus according to claim 1, wherein a mixed water-methanol gas is introduced simultaneously with or after the introduction of air.

[Claim 3] A method of starting a methanol reforming apparatus according to claim 1 or 2, wherein the amounts to be introduced are controlled so that the molar ratio of water/methanol falls within a range of 1.0-2.0 at a time when the concentration of air at the inlet of the catalyst has decreased to 50% by mole or lower.

[Claim 4] An apparatus for supplying a fuel to a methanol reforming apparatus that generates a hydrogen-rich gas by reacting a mixed gas of water, methanol and air on a catalyst, comprising:

a mixed water-methanol solution tank wherein the molar ratio of water/methanol is controlled to a predetermined value for use in reforming;

a mixed water-methanol solution tank wherein the molar ratio of water/methanol is controlled to 4.6 or higher; and

a switching means that switches the mixed water-methanol solution tanks used as a



fuel source according to the conditions of operation of the methanol reforming apparatus.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to method of starting a methanol reforming apparatus that generates a hydrogen enriched gas from water and methanol, and an apparatus for supplying a fuel to said methanol reforming apparatus.

[0002]

[Prior Art]

Fuel cells have been developed as a means for driving low-pollution vehicles and for supplying electric power to vehicles.

Hydrogen in the form of a compressed hydrogen gas or liquid hydrogen is convenient as the energy source for the fuel cell, but there are problems regarding to safety and the ease of handling. Thus there is a demand for a hydrogen supply apparatus having higher safety.

Recently, technologies for preparing hydrogen enriched gas by reforming alcohol or hydrocarbons using a catalyst have been intensively studied and developed, and various catalysts and reaction apparatuses have been invented.

[0003]

An example of the reaction apparatus is a methanol reforming apparatus (hereinafter referred to as "reformer") 1 shown in FIG. 5. For supplying fuel to the reformer 1, methods are known such as separately providing a water tank and a methanol tank or separately providing a mixed water-methanol solution tank 2 and a methanol tank 3 in order to prevent water from freezing in cold climates, as disclosed in Japanese Patent Application, First Publication No. Hei 8-91804, wherein water and methanol are delivered from the two tanks

in a liquid state to an evaporator 4 to produce a mixed water-methanol gas which is then supplied to the reformer 1.

[0004]

[Problem to be Solved by the Invention]

However, when methanol, which has a low flash point and a low ignition point, is reformed, particularly when employing the autothermal reaction process, wherein a partial oxidization reaction and steam reforming reaction are carried out at the same time, methanol vapor and air coexist on a catalyst that has a high temperature, and therefore the reforming process must be carried out in a strictly controlled system to prevent the reaction from proceeding at an excessively high rate.

[0005]

Specifically, the mixing ratio of water, methanol and air must not be within a range in which the reaction proceeds at an excessively high rate (hereinafter this range is referred to as "high-rate reaction region"), and the amounts of these materials to be introduced must be strictly controlled.

Before starting the operation of the reformer, on the other hand, the reformer must be warmed and particularly the catalyst layer must be warmed by a heating means until the catalyst becomes active. Hot air or electric heating have been normally used for this purpose.

[0006]

While water, methanol and air are introduced into the catalyst after the warm-up operation, it is very difficult to control the mixing ratio of the three components so as to avoid the high-rate reaction region. To get around this difficulty, such measures have been taken in the prior art as changing the order of introducing the materials, for example, introducing air

after water and methanol have been introduced.

In practice, such measures involve the problems that it takes a long time to start the operation or that special means are required to warm up the catalyst.

[0007]

To prevent water from freezing in a cold climate, it is more advantageous to provide a mixed water-methanol solution tank 2 than to separately provide a water tank and a methanol tank. Actually, however, it is a common practice to provide a methanol tank 3 in addition to the mixed water-methanol solution tank 2 and to control the mixing ratio using the methanol tank 3 in order to obtain the desired ratio of water and methanol.

[0008]

As a consequence, there was a problem in that a mixed water-methanol gas having a ratio outside of the high-rate reaction region cannot be immediately supplied during the starting/stopping operations of the reformer 1, when the control tends to be unstable.

A similar problem can also be expected in the case that a water tank and a methanol tank are separately provided.

[0009]

The present invention has been made in consideration of the problems described above, and an object thereof is to provide a starting method that allows it to quickly shift to the reforming process after warming up the catalyst.

[0010]

Another object of the present invention is to provide a fuel supplying apparatus that is capable of maintaining a stable supply of mixed water-methanol solution while preventing water from freezing in a cold climate, and is capable of immediately supplying mixed water-methanol gas that has composition which does not fall in the high-rate reaction region during

a starting/stopping operation when the control tends to be unstable.

[0011]

[Means for Solving the Problem]

According to the present invention, in order to achieve the objects described above, first a catalyst layer (reforming catalyst layer 41 in FIG. 1) is heated to an activation temperature. An external heat source such as an electric heater may be used or a flow of heating gas such as air that has been heated to a predetermined temperature may be used for heating the catalyst layer.

When the catalyst layer (reforming catalyst layer 41) has been heated to the predetermined activation temperature, a mixed water-methanol gas is supplied as the fuel, thereby carrying out the reforming reaction.

[0012]

The reaction can be started smoothly by controlling the water, methanol and air gas mixture so as to avoid the high-rate reaction region when introducing the fuel.

The present inventors have found, from the three-component mixture phase diagram of water, methanol and air shown in FIG. 2, that the reaction can be started smoothly without allowing the reaction to proceed at a high rate by controlling the amount of mixed gas of water, methanol and air introduced so as to keep the molar ratio of water/methanol (hereinafter referred to as S/C ratio) to 4.6 (= 82% by mole/18% by mole) or higher, or to keep the molar ratio of air/methanol (hereinafter referred to as A/C ratio) to 1.5 (= 60% by mole/40% by mole) or lower. In this drawing, the hatched portion is the high-rate reaction region.

[0013]

The present inventors have also found that, once the starting operation has been

completed, the reaction does not proceed at a high rate even when the S/C ratio of the mixed water-methanol gas is changed within a range of 1.0-2.0 after the air concentration at the inlet of the catalyst layer (reforming catalyst layer 41) has decreased to 50% by mole or lower.

Based on the facts described above, the present invention makes it possible to control the mixed water-methanol gas so as to avoid the high-rate reaction region when it is introduced into the apparatus when the oxygen concentration is high immediately after starting the operation. It is also possible to quickly shift to the reforming process after the starting operation has been completed.

[0014]

According to the present invention, two tanks are provided separately: a mixed water-methanol solution tank (27a) wherein the mixing ratio of water and methanol is controlled to within a range of S/C ratios (for example, 1.0-2.0) that are used in a normal reforming process, and a mixed water-methanol solution tank (27b) wherein mixing ratio of water and methanol is controlled to within a range of S/C ratios (4.6 or higher) used when starting or stopping the reforming process.

The two mixed water-methanol solution tanks (27a, 27b) are connected with respective liquid transport tubes to an evaporator (22) that is located in a stage prior to the catalyst layer of the reformer (23), while the source for supplying the fuel to the evaporator (22) is switched by means of three way valves (51, 52) or the like.

[0015]

Since the mixed water-methanol solution used in the normal reforming process is supplied from the mixed water-methanol solution tank (27a) where the S/C ratio is controlled to within a range of 1.2-2.0, a mixed water-methanol gas having the ideal molar ratio can be immediately supplied to the reformer (23) when the operation shifts from the start-up to the

normal reforming process.

The S/C ratio can be set to any desired value according to the characteristics of the reforming catalyst.

[0016]

The mixed water-methanol solution used mainly when starting or stopping the reformer (23) is supplied from the other mixed water-methanol solution tank (27b) where the S/C ratio is controlled to 4.6 or higher. Thus the composition of the mixed gas of water, methanol and air that is supplied to the reformer (23) does not fall in the high-rate reaction region during the starting/stopping operation when the control tends to be unstable.

[0017]

This is because, as will be apparent from the three-component phase diagram of FIG. 2, the danger of falling in the high-rate reaction region can be avoided regardless of the mixing conditions as long as the S/C ratio is controlled to 4.6 or higher.

While the composition of the fuel departs more from the high-rate reaction region as the S/C ratio becomes higher, the S/C ratio is preferably set to 4.6 since the mixing ratio should have a value that best facilitates the starting and stopping of the reformer (23).

[0018]

#### [Embodiments of the Invention]

Preferred embodiments of the present invention will now be described below with reference to the accompanying drawings.

#### (First Embodiment)

FIG. 1 shows a system for supplying fuel to a fuel cell in an electric vehicle, where the reference numeral 10 denotes a fuel cell.

The fuel cell 10 generates electricity by using hydrogen and oxygen that is taken from

air as the fuel.

A hydrogen supply system and an air supply system for the fuel cell 10 will be described below.

[0019]

(Hydrogen supply system)

The hydrogen supply system comprises a combustion device 21, an evaporator 22, a reformer (methanol reforming apparatus) 23, a CO eliminator 24, a starting heater 25, heat exchangers 26a, 26b, mixed water-methanol solution tanks 27a, 27b and a methanol tank 28 as major components.

[0020]

The combustion device 21 has an electric heater 31 serving as an ignition device, a combustion catalyst 32 that maintains the state of combustion and a temperature sensor 33 that monitors the temperature inside of the apparatus, wherein methanol supplied from the methanol tank 28 is burned with the air supplied from the air supply system, thereby generating a combustion gas used to warm up the evaporator 22 which evaporates the mixed water-methanol solution that is supplied to the evaporator 22.

[0021]

Connected to the combustion device 21 is an off gas tube 34 provided for the purpose of reusing the off gas that includes hydrogen-rich gas, which is generated in the reformer 23 in the period from the startup to the normal operation, and unreacted hydrogen, which is discharged from the fuel cell 10 during stationary operation, as the fuel for combustion.

[0022]

In the evaporator 22, the mixed water-methanol solution that has been supplied from the mixed water-methanol solution tank 27a where the S/C ratio is controlled to 1.5 or from

the mixed water-methanol solution tank 27b where the S/C ratio is controlled to 4.6 is sprayed from a nozzle and evaporated by the combustion gas supplied from the combustion device 21, thereby generating the mixed water-methanol gas.

The evaporator 22 is provided with a temperature sensor 36 for monitoring the temperature inside of the device.

[0023]

Installed in the reformer 23 is a reforming catalyst 41 comprising a honeycomb structure of which surface is coated with a catalyst such as Ni, Ru, Rh, Cu-Zn or the like, so that the mixed water-methanol gas supplied from the evaporator 22 is brought onto the reforming catalyst layer 41 to generate hydrogen-rich gas.

The reforming catalyst layer 41 has an O<sub>2</sub> sensor 42 installed at the inlet thereof, and a temperature sensor 43 installed inside of the reforming catalyst layer 41.

[0024]

In the reformer 23, the autothermal reforming reaction takes place as follows.



The reaction scheme (1) represents the steam reforming reaction by methanol and water that produces the target product of hydrogen.

The reaction scheme (2) represents the reaction of partial oxidization of methanol that produces heat by oxidization reaction which provides for the heat needed in the endothermic reaction represented by reaction scheme (1).

[0025]

In the reformer 23, in addition to the reactions represented by the reaction schemes (1) and (2), a trace amount of carbon monoxide is generated in an inevitable reaction of methanol



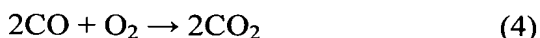
decomposition represented as follows.



The carbon monoxide deteriorates Pt catalyst provided in the fuel cell 10 and leads to lower efficiency of power generation and shortens the service life of the cell, and is therefore removed by the CO eliminator 24 installed in a latter stage.

[0026]

The CO eliminator 24 has a selective oxidization catalyst layer made by coating the surface of a honeycomb structure with a catalyst such as Pt or Ru. When hydrogen-rich gas generated by the reformer 23 is supplied, the carbon monoxide is removed from the hydrogen-rich gas in the following reaction of selective oxidization of CO.



[0027]

Installed between the reformer 23 and the CO eliminator 24 is the heat exchanger 26a provided for the purpose of cooling down the hydrogen-rich gas generated by the reformer 23 thereby protecting the selective oxidization catalyst in the CO eliminator 24 from thermal damage. Similarly installed between the CO eliminator 24 and the fuel cell 10 is the heat exchanger 26b provided for the purpose of cooling down the hydrogen-rich gas supplied from the CO eliminator 24 thereby protecting the Pt catalyst in the fuel cell 10 from thermal damage.

[0028]

Valves 51, ..., pumps 55, ... installed in the hydrogen supply system are controlled by an ECU (Electronic Control Unit) 45.

The ECU 45 sends command signals to the valves 51, ..., the pumps 55, ... in accordance to the output signals from the O<sub>2</sub> sensor 42 and the temperature sensor 43, thereby

causing these devices to function.

The ECU 45 functions also as means for switching the mixed water-methanol solution tanks 27a, 27b that are used as fuel supply sources.

[0029]

(Air supply system)

The air supply system comprises a PCU 61, a drive motor 62, a super charger 63, an inter cooler 64 and filters 65a, 65b as major components, and supplies air, that is introduced from the outside, to the fuel cell 10, the combustion device 21 and the starting heater 25.

Main function of the PCU 61 is to adjust the output of the drive motor 62, by regulating the electric power supplied from the fuel cell 10 and supplies the regulated power to the drive motor 62.

[0030]

The super charger 63 compresses the air taken from the outside through the filter 65a, via a resonator 66.

The inter cooler 64 is provided for cooling down the air that has been heated through compression by the super charger 63. The cooled air passes through the filter 65b, which is installed in the latter stage of the inter cooler 64, and is supplied to the fuel cell 10, the combustion device 21 and the starting heater 25.

[0031]

Now the method of starting the reformer 23 according to this embodiment will be described below.

To start the apparatus in cold state, it is necessary to warm up the evaporator 22, the reformer 23 and the CO eliminator 24 of the hydrogen supply system. For this reason, the valve 53 is opened to spray methanol into the combustion device 21 and air that includes

oxygen is supplied from the air supply system to burn the methanol, while the combustion gas generated thereby is supplied to evaporator 22 for the warming up thereof.

Air is supplied also to the starting heater 25, while the air heated therein is sent to the reformer 23 thereby warming up the reformer 23 and the CO eliminator 24 installed downstream thereof.

[0032]

When the evaporator 22 has been heated to a temperature high enough to evaporate the mixed water-methanol solution and the reformer 23, the reforming catalyst 41 in the CO eliminator 24 and the selective oxidization catalyst layer have reached the activation temperature, the valves 53, 54 are closed, while spraying of methanol into the combustion device 21 and the supply of air to the starting heater 25 are stopped.

At this time, the reformer 23 is supplied only with air from the air supply system.

The combustion device 21 is also supplied only with air from the air supply system, while the state of combustion by the combustion catalyst 32 is maintained.

[0033]

Then the valve 51 is opened with the valve 52 is left closed, while the pump 55 supplies the mixed water-methanol solution, with the S/C ratio therein being controlled to 4.6, from the mixed water-methanol solution tank 27b to the evaporator 22, so that the mixed water-methanol solution is sprayed from the nozzle into the evaporator 22.

In the evaporator 22, the mixed water-methanol solution is evaporated by the combustion gas supplied from the combustion device 21, thereby generating the mixed water-methanol gas which is supplied to the reformer 23.

In the reformer 23, the mixed water-methanol gas is passed through the reforming catalyst 41 to produce hydrogen-rich gas through the reactions of the reaction schemes (1)

and (2).

[0034]

At this time, according to the three-component mixture phase diagram of water, methanol and air of FIG. 2, smooth startup is achieved provided that the S/C ratio of the mixed water-methanol gas is 4.6 which means the mixing ratio is outside of the high-rate reaction region.

[0035]

The reforming process enters the steady state upon lapse of some time after starting the reformer 23.

During this transition of the state of operation, it is necessary to change the S/C ratio from 4.6, which is the value for starting the operation, to 1.0 to 2.0 which is a range of values for normal reforming operation.

Accordingly, the valve 51 is closed and the valve 52 is opened when the air concentration measured by the O<sub>2</sub> sensor 42 installed at the inlet of the reforming catalyst layer 41 has decreased to 50% by mole or less.

[0036]

Then the pump 56 supplies the mixed water-methanol solution with the S/C ratio controlled to 1.5 from the mixed water-methanol solution tank 27a to the evaporator 22, so that the mixed water-methanol solution is sprayed from the nozzle into the evaporator 22.

In the evaporator 22, the mixed water-methanol solution is evaporated by the combustion gas supplied from the combustion device 21 to generate the mixed water-methanol gas which is supplied to the reformer 23.

[0037]

The hydrogen-rich gas produced in the reformer 23 is cooled down from about 300°C

to about 100°C while passing through the heat exchanger 26a, to be supplied to the CO eliminator 24.

In the CO eliminator 24, carbon monoxide is removed in the reaction of the reaction scheme (4) by passing the hydrogen-rich gas through the selective oxidization catalyst layer.

The hydrogen-rich gas with CO removed therefrom is cooled down from about 180°C to about 80°C while passing through the heat exchanger 26b, and then supplied to the fuel cell 10 to be used in power generation.

[0038]

On the other hand, the air that has been introduced through the resonator 66 and the filter 65a into the air supply system is compressed in the super charger 63 and is then cooled down in the inter cooler 64, before passing through the filter 65b and supplied to the fuel cell 10 and the combustion device 21.

[0039]

Oxygen included in the air that is supplied to the fuel cell 10 is used, together with hydrogen supplied from the hydrogen supply system, for power generation.

The air supplied to the combustion device 21 is used for generating the combustion gas.

The off gas that includes the unreacted hydrogen discharged from the fuel cell 10 is returned to the combustion device 21 through the off gas tube 34, and is reused as the fuel for combustion.

[0040]

(Second Embodiment)

The second embodiment of the present invention will be described below with reference to FIG. 3. Identical components to those shown in FIG. 1 will be assigned with

the same reference numerals and description thereof will be omitted.

This embodiment is similar to First Embodiment, except for a part of the hydrogen supply system and a part of the air supply system which are different from those of First Embodiment.

[0041]

The hydrogen supply system has a condenser 71 and an S/C control tank 72 instead of the mixed water-methanol solution tank 27b where the S/C ratio is controlled to 4.6 shown in FIG. 1.

The condenser 71 recovers water, that is generated in the reaction and combustion in the fuel cell 10, from the evaporator 22.

In the S/C control tank 72, mixed water-methanol solution (S/C ratio 4.6 or higher) used in start/stop operation is prepared from the mixed water-methanol solution (S/C ratio 1.5) supplied from the mixed water-methanol solution tank 27a and the recovered water supplied from the condenser 71.

[0042]

S/C ratio of the liquid in the S/C control tank 72 is constantly monitored by a methanol sensor 73 of which signal is sent to the ECU 45.

The ECU 45 controls the extents of opening of valves 75, 76 according to the signal.

After the preparation of the mixed water-methanol solution by the S/C control tank 72 and when the operation is stopped, excessive recovered water in the condenser 71 is discarded.

[0043]

The air supply system has an air supply line 81 connected to the evaporator 22.

Accordingly, the evaporator 22 also serves as a heater that heats the air supplied via

the air supply line 81.

Consequently, in this embodiment, the starting heater 25 shown in FIG. 1 is not necessary since the reformer 23 can be warmed up by the heated air.

[0044]

With the constitution described above, too, the mixed water-methanol solution tank 27a for the normal reforming process and the S/C control tank 72 for the start/stop operation can be switched according to the state of operation of the reformer 23, and therefore it is made possible to maintain stable supply of mixed water-methanol solution while preventing water from freezing in a cold climate, and is capable of immediately supplying mixed water-methanol gas that has composition outside of the high-rate reaction region during starting/stopping operation of the reformer 23 when the control tends to be unstable.

[0045]

(Example 1)

Using a test apparatus equipped with a reactor tube made of quartz having inner diameter of 20 mm that was filled with 9.2 g of methanol reforming catalyst pellets including Cu, Zn and Al in the ratio of 1.3: 1: 0.05, heated air was introduced to the catalyst at a flow rate of 40 ml/min thereby heating the catalyst to 230°C.

After making sure that the catalyst has been heated to 230°C, the mixed water-methanol solution of which S/C ratio was regulated to 1.5 was supplied to the evaporator, and the mixed water-methanol gas generated therein was supplied to the catalyst at a flow rate of 1.8 ml/min, while recording the changes in the catalyst temperature immediately after supplying the gas (plots ◆ in FIG. 4).

[0046]

(Example 2)

Using the same test apparatus as in Example 1, heated air was introduced to the catalyst at a flow rate of 40 ml/min to heat the catalyst to 230°C.

After stopping the introduction of air and making sure that the catalyst was heated to 230°C, the mixed water-methanol solution similar to that of Example 1 was supplied to the evaporator, and the mixed water-methanol gas generated therein was supplied to the catalyst at a flow rate of 1.8 ml/min, while recording the changes in the catalyst temperature immediately after supplying the gas. Then the introduction of air was resumed at a flow rate of 40 ml/min while recording the changes in the catalyst temperature immediately after the introduction (plots □ in FIG. 4).

[0047]

(Example 3: present invention)

Using the same test apparatus as in Example 1, heated air was introduced to the catalyst at a flow rate of 40 ml/min to heat the catalyst to 230°C.

After making sure that the catalyst was heated to 230°C, the mixed water-methanol solution of which S/C ratio was regulated to 4.6 was supplied to the evaporator, and the mixed water-methanol gas generated therein was supplied to the catalyst at a flow rate of 1.8 ml/min, while recording the changes in the catalyst temperature immediately after supplying the gas (plots △ in FIG. 4).

[0048]

When the mixed water-methanol gas having a low value of S/C ratio was supplied to the heated catalyst under the condition of introducing air as in Example 1, it was confirmed that the catalyst temperature rose rapidly and it took a long time to stabilize the reaction, while the danger of thermal runaway increased.

This is because the exothermic reaction of the reaction scheme (2) proceeds at a



higher rate than the endothermic reaction of the reaction scheme (1).

[0049]

Similarly, when the mixed water-methanol gas having a low value of S/C ratio was supplied while stopping the introduction of air as in Example 2, it was confirmed that the catalyst temperature rose rapidly, although the peak temperature as high as in Example 1 was not reached.

This is because the exothermic reaction of the reaction scheme (2) proceeds rapidly as the system already includes air even when the air is not flowing.

[0050]

However, only the endothermic reaction of the reaction scheme (1) proceeds thereafter because of the lack of air, resulting in a problem that the catalyst temperature drops quickly.

Even when the introduction of air is resumed, the catalyst temperature rises rapidly, although the peak temperature as high as in the case of supplying the mixed water-methanol gas is not reached.

As described above, unstable condition wherein the temperature repeatedly fluctuates continues for several minutes in Example 2.

[0051]

In contrast to Examples 1 and 2, when the S/C ratio was set to a value outside of the high-rate reaction region in the early stage of introducing the mixed water-methanol gas as in Example 3, excessive increase in the catalyst temperature and fluctuation of the temperature could be suppressed and the danger of thermal runaway could be avoided. Consequently, switching to the mixed water-methanol solution of the desired value of S/C ratio could be quickly provided for.

This is because the endothermic reaction of the reaction scheme (1) proceeds predominantly over the exothermic reaction of the reaction scheme (2) due to the supply of water-rich fuel, thus maintaining the thermal balance.

[0052]

The present invention is not limited to the embodiments described above, and the reforming catalyst 41 may be warmed up by electric heating instead of air heating.

As will be apparent from FIG. 2, the process can be started smoothly outside of the high-rate reaction region similarly to the above also by controlling the mixing ratio of water, methanol and air so that the A/C ratio becomes 1.5 or lower.

[0053]

This is because lower ratio of oxygen is introduced compared to methanol, resulting in less amount of heat generated in the reaction of the reaction scheme (2).

The S/C ratio may also be controlled to be 4.6 or higher while the A/C ratio is set to 1.5 or lower, as a matter of course.

[0054]

#### [Advantage Effects of the Invention]

The present invention has the following effects.

(a) Since the method controls the amount of the mixture of water, methanol and air that is introduced so that the molar ratio of water/methanol becomes 4.6 or higher and/or the molar ratio of air/methanol becomes 1.5 or lower when starting the reformer, the reaction can be started smoothly with a mixing ratio which is clear of the high-rate reaction region even at the start of operation when the oxygen concentration is high.

[0055]

(b) Since the mixed water-methanol gas is introduced simultaneously with or after the

introduction of air, the starting time can be made shorter.

(c) Since the amount of fuel introduced is controlled so that the molar ratio of water/methanol is within a range of 1.0-2.0 once the concentration of air at the inlet of the reforming catalyst has decreased to 50% by mole or lower, changing from the start-up operation to the reforming operation can be carried out quickly without falling in the high-rate reaction region.

[0056]

(d) A switching means is provided to switch the mixed water-methanol solution tank to be used as the source of fuel supply, between the mixed water-methanol solution tank wherein the molar ratio of water/methanol is controlled to the predetermined concentration used in the reforming process, and the mixed water-methanol solution tank wherein the molar ratio of water/methanol is controlled to 4.6 or higher, in accordance to the operating conditions of the reformer. Thus a stable supply of the mixed water-methanol solution is made possible while preventing the water from freezing in a cold climate.

Also, a mixed water-methanol gas of a composition that is outside of the high-rate reaction region can be immediately supplied during start/stop of the reformer when the control tends to be unstable.

#### [Brief Description of the Drawings]

[FIG. 1] FIG. 1 shows a system for supplying fuel to a fuel cell in an electric vehicle according to First Embodiment of the present invention.

[FIG. 2] FIG. 2 is a three-component mixture phase diagram of water, methanol and air.

[FIG.3] FIG. 3 shows a system for supplying fuel to a fuel cell in an electric vehicle according to Second Embodiment of the present invention.

[FIG. 4] FIG. 4 shows a change in the temperature of a catalyst measured using a test apparatus.

[FIG. 5] FIG. 5 shows a system for supplying fuel to a fuel cell in an electric vehicle according to a conventional example.

[Description of Reference Symbols]

23: reformer (methanol reforming apparatus); 27a and 27b: mixed water-methanol solution tank; 41: reforming catalyst; 45: ECU (Electronic Control Unit)

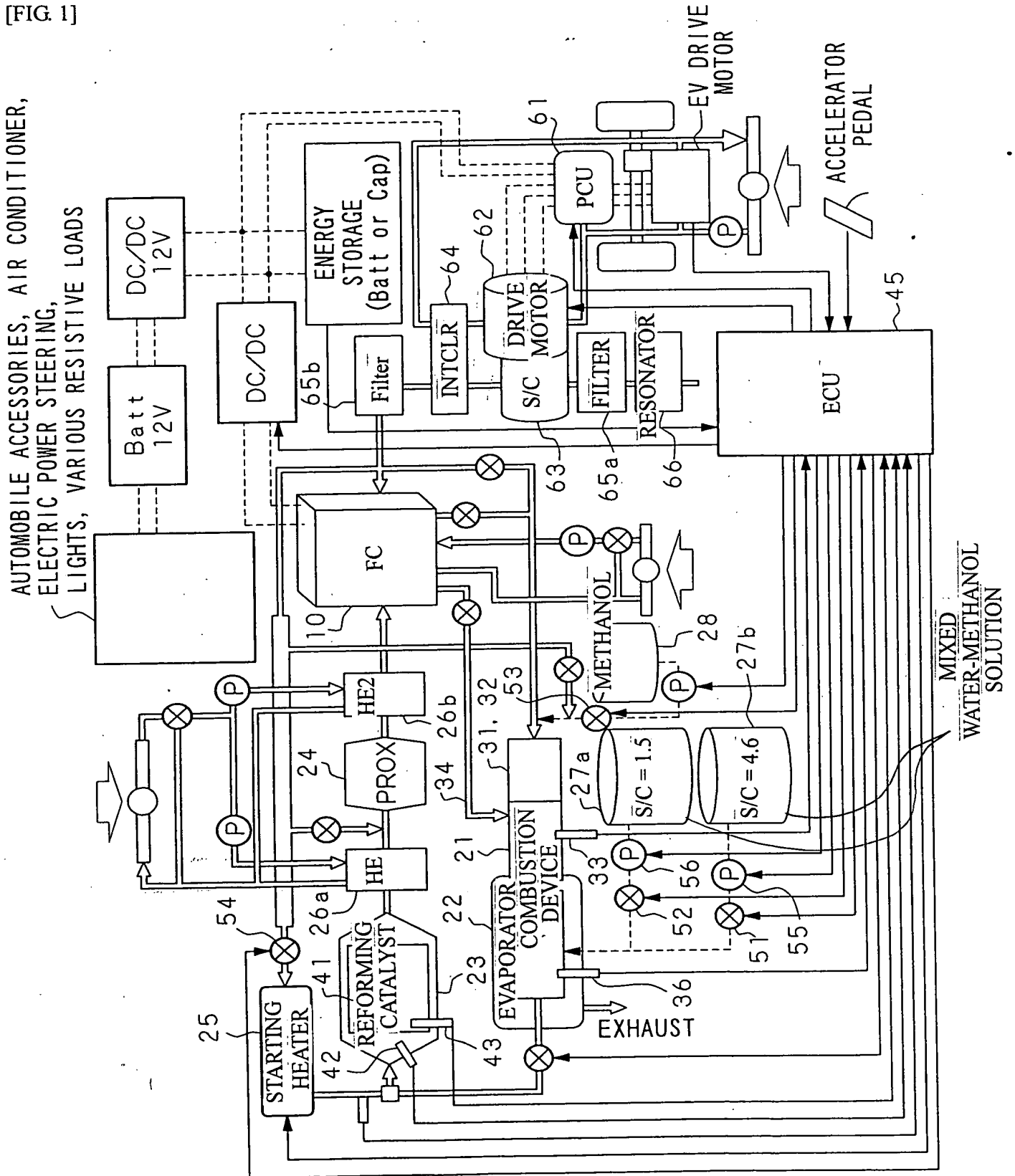
[Document Type] Abstract

[Abstract]

[Problem to be Solved by the Invention] To provide a starting method that allows it to quickly shift to the reforming process after warming up the catalyst.

[Means for Solving the Problem] According to the present invention, in the method of starting a methanol reforming apparatus, a reforming catalyst layer (41) which is provided on a reformer (23) is heated to a predetermined activation temperature, next an air which is needed to the reaction is supplied, and then a mixed water-methanol gas is supplied. The amounts to be introduced are controlled so that the molar ratio of water/methanol is 4.6 or higher and/or the molar ratio of air/methanol is 1.5 or lower. The molar ratio of water/methanol is fallen within a range of 1.0-2.0 when the concentration of air at the inlet of the catalyst has decreased to 50% by mole or lower. Two tanks are provided separately: a mixed water-methanol solution tank (27a) where the molar ratio of water/methanol is controlled to within the range of 1.0-2.0, and a mixed water-methanol solution tank (27b) where the molar ratio of water/methanol is controlled to within the range of 4.6 or higher. These tanks (27a) and (27b) are switched according to the conditions of operation of the reformer (23) to switch the molar ratio of water/methanol.

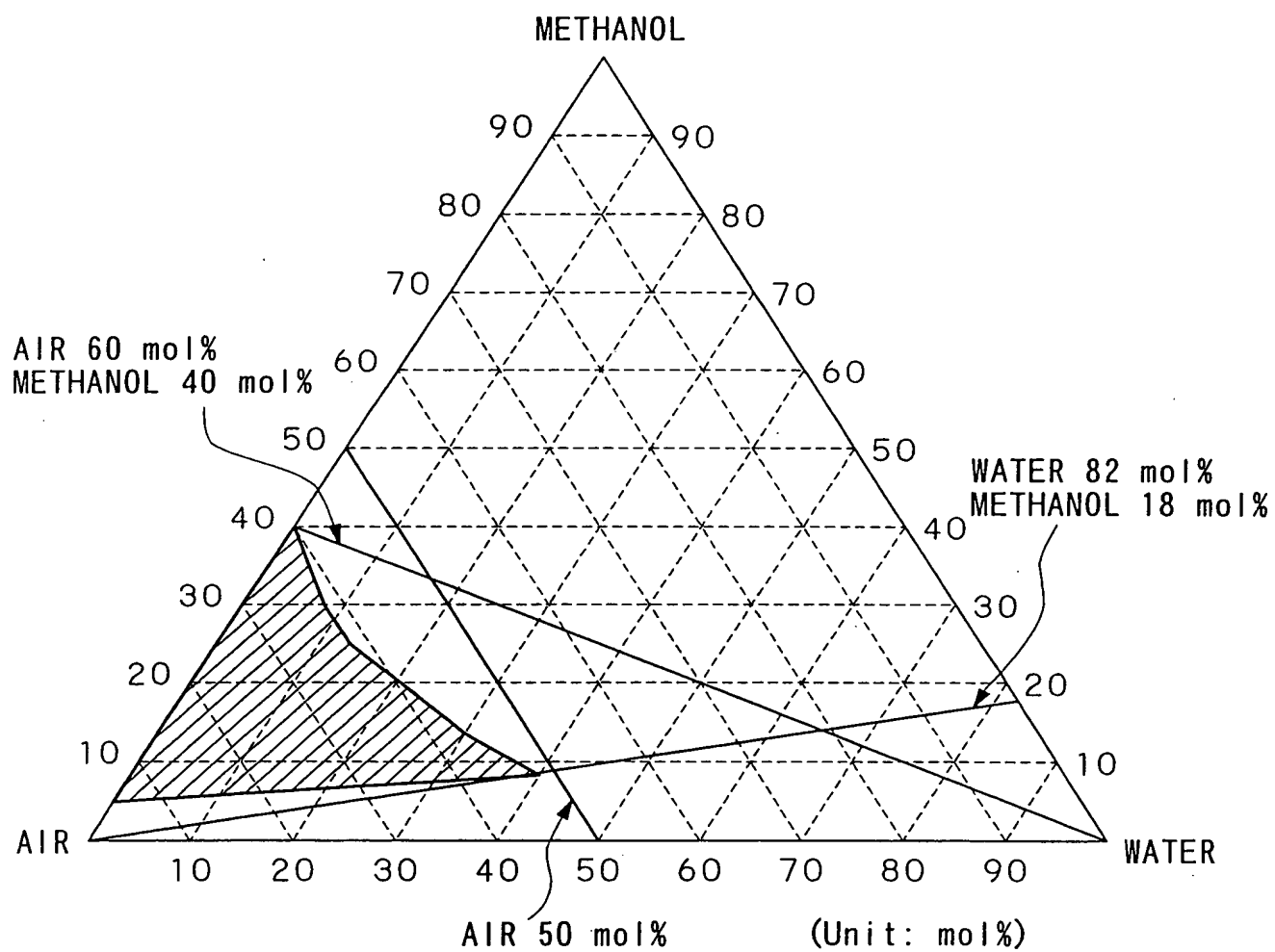
[FIG. 1]



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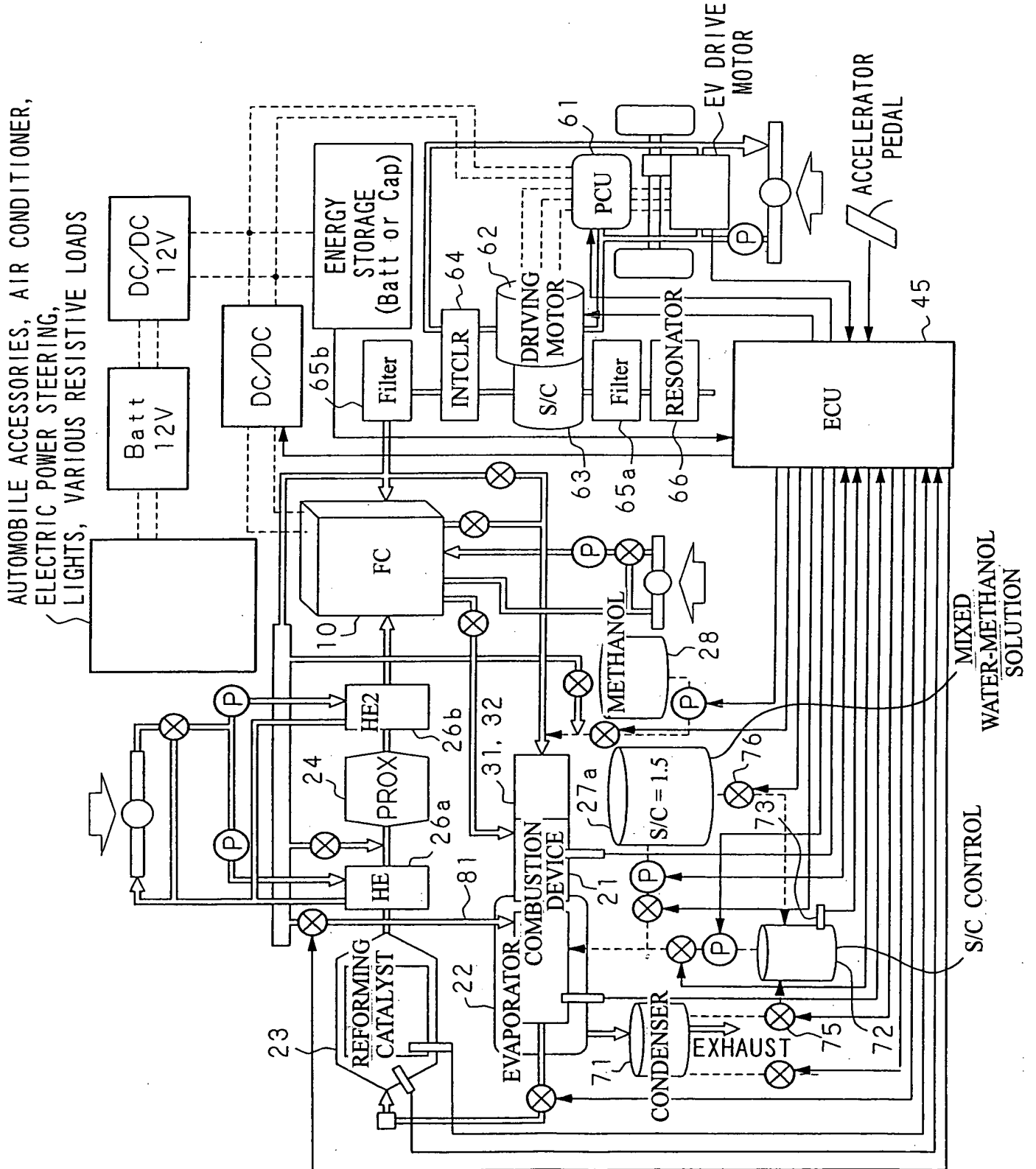
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[FIG. 2]



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[FIG. 3]





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[FIG. 4]

